

# On the Insignificance of Photochemical Hydrocarbon Aerosols in the Atmospheres of Close-in Extrasolar Giant Planets

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## ABSTRACT

The close-in extrasolar giant planets (CEGPs) reside in irradiated environments much more intense than that of the giant planets in our solar system. The high UV irradiance strongly influences their photochemistry and the general current view believed that this high UV flux will greatly enhance photochemical production of hydrocarbon aerosols. In this letter, we investigate hydrocarbon aerosol formation in the atmospheres of CEGPs. We find that the abundances of hydrocarbons in the atmospheres of CEGPs are significantly less than that of Jupiter except for models in which the CH<sub>4</sub> abundance is unreasonably high (as high as CO) for the hot (effective temperatures  $\gtrsim 1000$  K) atmospheres. Moreover, the hydrocarbons will be condensed out to form aerosols only when the temperature-pressure profiles of the species intersect with the saturation profiles—a case almost certainly not realized in the hot CEGPs atmospheres. Hence our models show that photochemical hydrocarbon aerosols are insignificant in the atmospheres of CEGPs. In contrast, Jupiter and Saturn have a much higher abundance of hydrocarbon aerosols in their atmospheres which are responsible for strong absorption shortward of 600 nm. Thus the insignificance of photochemical hydrocarbon aerosols in the atmospheres of CEGPs rules out one class of models with low albedos and featureless spectra shortward of 600 nm.

*Subject headings:* planetary systems—radiative transfer—stars: atmosphere—stars: individual (HD 209458)

## 1. Introduction

Hazes and clouds<sup>1</sup> in the atmospheres of jovian planets can strongly affect the ability to determine atmospheric composition at ultraviolet to infrared wavelengths. At wavelengths shorter than  $\sim$ 600 nm, the atmospheric line features in the jovian planets are “washed out” by the hazes/clouds in the atmospheres of planets (e.g., Karkoschka & Tomasko 1993; Karkoschka 1998). The main chemical compositions of the hazes/clouds on Jupiter are believed to be  $\text{H}_2\text{O-NH}_3$ ,  $\text{NH}_4\text{SH}$ ,  $\text{NH}_3$ ,  $\text{N}_2\text{H}_4$ , and hydrocarbons from several bar to  $\sim$ 0.1 mbar (Weidenschilling & Lewis 1973; Strobel 1983; West et al. 1986; Pryor & Hord 1991; Gladstone et al. 1996; Banfield et al. 1998a,b; Wong et al. 2003). Saturn may have a composition profile similar to Jupiter since they have similar 300-1000 nm spectra (e.g., Karkoschka 1998). Saturn’s albedo has been successfully modelled by assuming a dichotomy in the aerosol distribution between the troposphere and stratosphere, where the number density of aerosols is much lower in the stratosphere (Karkoschka & Tomasko 1993). It is found that the stratospheric aerosols are very dark at  $\sim$ 300 nm, implying the presence of hydrocarbon aerosols.

Since the recent increase in sample size of extrasolar planets (e.g., Udry et al. 2002; Butler et al. 2003), the planetary formation environment has been statistically analyzed, although not conclusively (Fischer et al. 2002; Santos et al. 2003). The close-in extrasolar giant planets (CEGPs, with semi-major axes  $\lesssim$  0.05 AU, also known as “hot Jupiters”) are of particular interest since they have more active chemical processes in their atmospheres (e.g., Liang et al. 2003) and the evolution of the atmospheres can currently be studied observationally (e.g., Vidal-Madjar et al. 2003, 2004). A number of simulations in the atmospheres of CEGPs have been performed to study the albedos and reflection spectra by including the formation of high temperature condensates, such as silicates (e.g., Sudarsky et al. 2000; Seager et al. 2000). The importance and existence of the atmospheric aerosols have been addressed and discussed widely in recent years (e.g., Baraffe et al. 2003) and it is generally believed that more UV flux will result in more aerosols. The photochemistry in jovian atmospheres results in photochemical aerosols which significantly affect the ultraviolet-visible spectra and albedos; hence we were motivated to simulate the formation of various molecules, e.g., hydrocarbons, ammonia, and sulfuric acid, which are the possible sources of aerosols, in the atmospheres of CEGPs. In this letter, we focus on hydrocarbons and hydrocarbon aerosol formation.

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<sup>1</sup> “Hazes” refers to the diffuse and optically thin aerosol distribution, while “clouds” refers to the optically thick regions (West et al. 1986).

## 2. Model

A one-dimensional Caltech/Jet Propulsion Laboratory KINETICS model is applied to HD 209458b’s atmosphere, which is divided into 80 plane-parallel layers along the radial direction. The planet is probably tidally locked and our simulation is performed on the day side. The model assumes the four parent molecules: H<sub>2</sub>, CO, H<sub>2</sub>O, and CH<sub>4</sub>. The abundances of CO and H<sub>2</sub>O for the reference model (Model A) are  $3.6 \times 10^{-4}$  and  $4.5 \times 10^{-4}$ , respectively. The CH<sub>4</sub> abundance is taken to be  $3.9 \times 10^{-8}$ , which is the low bound predicted by Seager & Sasselov (2000). The temperature-pressure profiles are not certain, because the global circulation and high temperature condensation are not constrained in generating the model atmosphere. Our reference profile (solid curve in Figure 1) is a derivative of a cloud-free and high temperature condensation-free model. The stellar irradiance is assumed to be uniformly distributed over the whole planet; this gives the lower bound of the temperature profile in the atmosphere of HD 209458b. In view of the aforementioned uncertainty, two alternative temperature profiles, which assume the redistribution of the stellar irradiance evenly only on the day side, are examined (Barman et al. 2002; Fortney et al. 2003).

A one-dimensional, photochemical-diffusive, diurnally averaged numerical model for hydrocarbon photochemistry has been presented by Gladstone et al. (1996) in the atmosphere of Jupiter. In that study, important chemical cycles and pathways involving C<sub>1</sub>-C<sub>4</sub> species are identified. Included in this analysis are sensitivity studies on a standard reference model with respect to variations in the eddy-diffusion profile, solar flux, atomic hydrogen influx, latitude, temperature, and important chemical reaction rates. The model reproduces extensive observations of hydrocarbon species as well as He 584 Å and H Lyman- $\alpha$  airglow emissions on Jupiter. Due to the incomplete laboratory measurements of reaction rates and photodissociation quantum yields in the C<sub>3</sub> and higher hydrocarbons, we use a simplified version of the hydrocarbon photochemical model by Gladstone et al. (1996). The hydrocarbon chemistry up to the C<sub>2</sub> hydrocarbons is modelled thoroughly in the atmosphere of HD 209458b. The C<sub>1</sub> and C<sub>2</sub> hydrocarbons are the fundamental ingredient for building up complex hydrocarbons, e.g., benzene and polycyclic aromatic hydrocarbons (PAHs), through long chain polyynes and polymerization. The chemical pathways among the C<sub>1</sub> and C<sub>2</sub> in the atmospheres of CEGPs were first pointed out by Liang et al. (2003), which are fundamentally different from the pathways on the colder jovian planets (Gladstone et al. 1996). The full version of the hydrocarbon photochemical model is also verified. The oxygen related photochemistry is taken from Moses et al. (2000).

Figure 1 shows the temperature profiles for three models (Seager & Sasselov 2000; Barman et al. 2002; Fortney et al. 2003). For each case, we have examined five different initial chemical abundances for CH<sub>4</sub>, CO, and H<sub>2</sub>O as tabulated in Table 1. Due to the

unconstrained CH<sub>4</sub> abundance, we have varied it by several orders of magnitudes to study its sensitivity in the formation of hydrocarbons. However, we expect CO to be the dominant reservoir of carbon for the range of temperatures in the atmospheres of CEGPs and assume this in our reference Model A. The models of Barman et al. (2002) and Fortney et al. (2003) go only to 1 and 0.1  $\mu$ bar pressure levels, respectively: we assume the profiles are isothermal above these pressure levels. The parameters for the reference eddy-diffusion profile ( $\kappa = \kappa_0(n/n_0)^{-\alpha}$ , where  $n$  is number density) are taken to be  $\kappa_0 = 2.4 \times 10^7$  cm<sup>2</sup> s<sup>-1</sup>,  $n_0 = 5.8 \times 10^{18}$  cm<sup>-3</sup>, and  $\alpha = 5.6$ . We also varied  $\kappa_0$  and  $\alpha$  to test the sensitivity of the results on eddy-diffusion (see Table 2). The fiducial eddy-diffusion used here is consistent with the upper limit estimates from Showman & Guillot (2002).

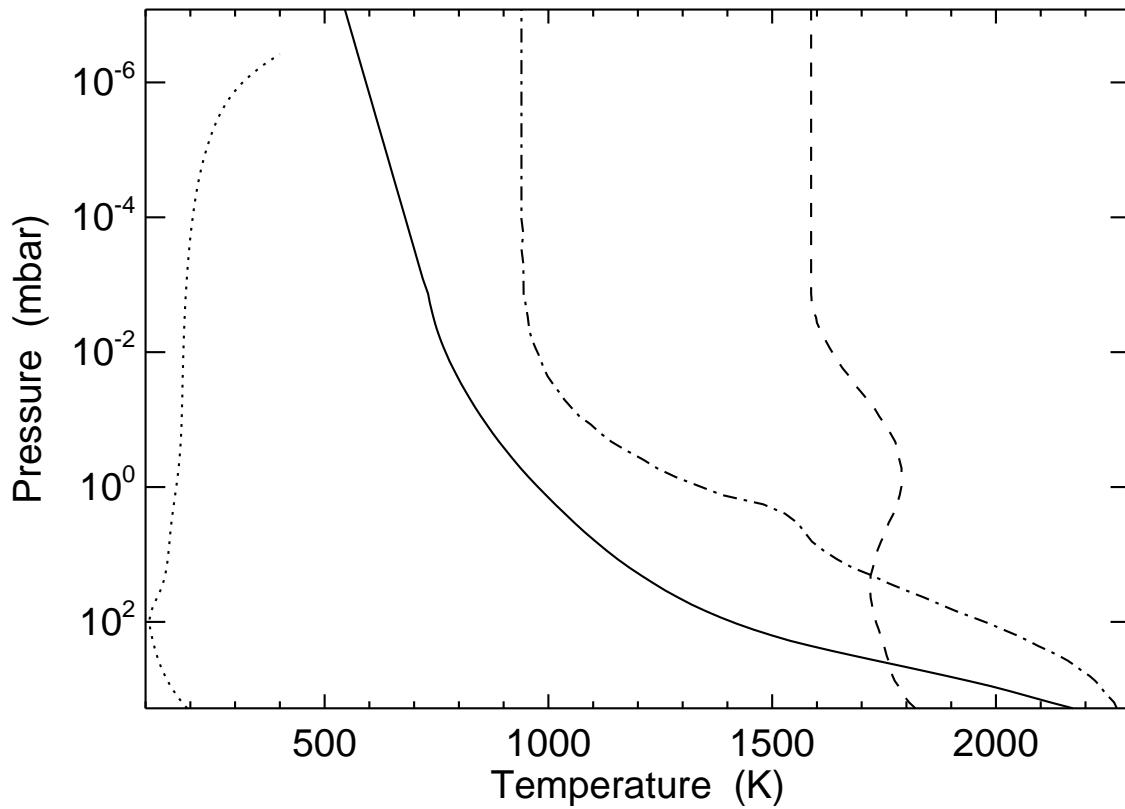


Fig. 1.— Vertical temperature profiles of the reference model (solid line), Barman et al. (2002, dashed line), Fortney et al. (2003, dash-dotted line), and Jupiter (dotted line). We assume the profiles of Barman et al. (2002) and Fortney et al. (2003) are isothermal above their reported pressure levels.

Table 1. Initial Chemical Abundances of CH<sub>4</sub>, CO, and H<sub>2</sub>O for Models A-E.

Model	CH <sub>4</sub>	CO	H <sub>2</sub> O
A	$3.9 \times 10^{-8}$	$3.6 \times 10^{-4}$	$3.6 \times 10^{-4}$
B	$3.9 \times 10^{-8}$	$3.6 \times 10^{-4}$	$3.6 \times 10^{-5}$
C	$3.9 \times 10^{-8}$	$3.6 \times 10^{-5}$	$3.6 \times 10^{-4}$
D	$3.9 \times 10^{-5}$	$3.6 \times 10^{-4}$	$3.6 \times 10^{-4}$
E	$3.6 \times 10^{-4}$	$3.6 \times 10^{-4}$	$3.6 \times 10^{-4}$

### 3. Results

Our modeling shows that gas phase hydrocarbons are most likely present in very low abundances in the atmospheres of CEGPs. This result is in contrast to the high abundances of hydrocarbons on the solar jovian planets. The vertical profiles of the hydrocarbons for various models are shown in Figure 3 and the maximum and column integrated hydrocarbons are tabulated in Table 2. The hydrocarbons are produced and concentrated mainly in the middle atmosphere, around 0.1 mbar. Because the framework of hydrocarbon formation on the jovian planets is well understood, we explain our results in comparison to the photochemical production of hydrocarbons on the jovian planets.

There are two known chemical schemes for the formation of hydrocarbons in the jovian atmospheres and their satellites. The first is via the synthesis of long chain polyynes from  $C_2H_2$  (Allen et al. 1980). The second is the polymerization of  $C_2H_2$  to form ring compounds (Wong et al. 2000). In both cases,  $C_2H_2$  plays a crucial role. Therefore, to explain why hydrocarbon aerosols are not formed in CEGPs, we have to explain why  $C_2H_2$  concentrations are so low. This is due primarily to the high temperatures in the atmospheres of CEGPs and secondarily to the high UV flux. Both the high temperatures and high UV fluxes are a direct consequence of the CEGPs' closer proximity to their parent stars.

One reason for low hydrocarbon abundances in CEGPs is because the abundance of  $CH_4$  is many orders of magnitudes lower than that in the jovian atmospheres. The  $CH_4$  abundance is important because in the jovian atmospheres hydrocarbon formation is driven by the photodissociation of  $CH_4$  and the subsequent reactions of the products (e.g., Gladstone et al. 1996). The three species,  $C_2H_2$ ,  $C_2H_4$ , and  $C_2H_6$ , are important for forming more complex hydrocarbons and hydrocarbon aerosols. The primary reservoir of C in CEGPs is CO, not  $CH_4$ , as in the jovian planets. This is due to the much higher temperatures in the atmospheres of CEGPs (effective temperatures  $\gtrsim 1000$  K) compared to Jupiter (effective temperature  $\sim 130$  K). Liang et al. (2003) showed that C compounds are initiated by C atoms produced by the photolysis of CO in the upper atmosphere. The hydrocarbons ( $C_2H_2$ ,  $C_2H_4$ , and  $C_2H_6$ ) are formed along with  $CH_4$  from the C atoms.

A second reason for the low abundance of hydrocarbons is that hydrogenation of  $C_2H_2$  to  $CH_4$  by the pathways given in Liang et al. (2003) (see also Chapter 5 of Yung and DeMore 1999) rapidly removes  $C_2H_2$ . As pointed out by Liang et al. (2003), the CEGPs have a high concentration of H atoms formed via an  $H_2O$  mediated process. Hydrogenation is the dominant removal process of  $C_2H_2$  in CEGPs and is driven by the high concentration of H atoms. Unlike the colder jovian atmospheres, the hydrocarbon loss via photolysis is minor in the atmospheres of CEGPs. A key reaction in hydrogenation of  $C_2H_2$  to  $CH_4$  is the

reaction  $\text{C}_2\text{H}_3 + \text{H}_2 \rightarrow \text{C}_2\text{H}_4 + \text{H}$ . The reaction that breaks the  $\text{H}_2$  bond is fast for the high temperatures in the atmospheres of CEGPs; however in the colder atmospheres of the jovian planets this reaction is the major bottleneck to hydrogenation of  $\text{C}_2\text{H}_2$ . Hydrogenation as a cause of low hydrocarbon abundances is therefore related to the high temperatures in the atmospheres of CEGPs which are hot enough not only for the rapid hydrogenation rate but also for  $\text{H}_2\text{O}$  to be present in vapor form. In contrast to the jovian planets and their satellites, water is frozen into ice and not available for photolysis.

To show the robustness of the result of low hydrocarbon abundances in the atmospheres of CEGPs, we varied the input parameters to our photochemical model. We find that over a broad range of input parameters, i.e., initial chemical abundances and temperature and eddy-diffusion profiles, the hydrocarbon formation in the atmospheres of CEGPs never exceeds that of Jupiter. In our model of an extremely abundant  $\text{CH}_4$  (Model E), the column integrated hydrocarbon is about 0.5 that of Jupiter's (see Table 2). However, this is an extreme and unlikely high  $\text{CH}_4$  abundance—the hot atmospheric temperatures favor CO as the dominant reservoir of C.

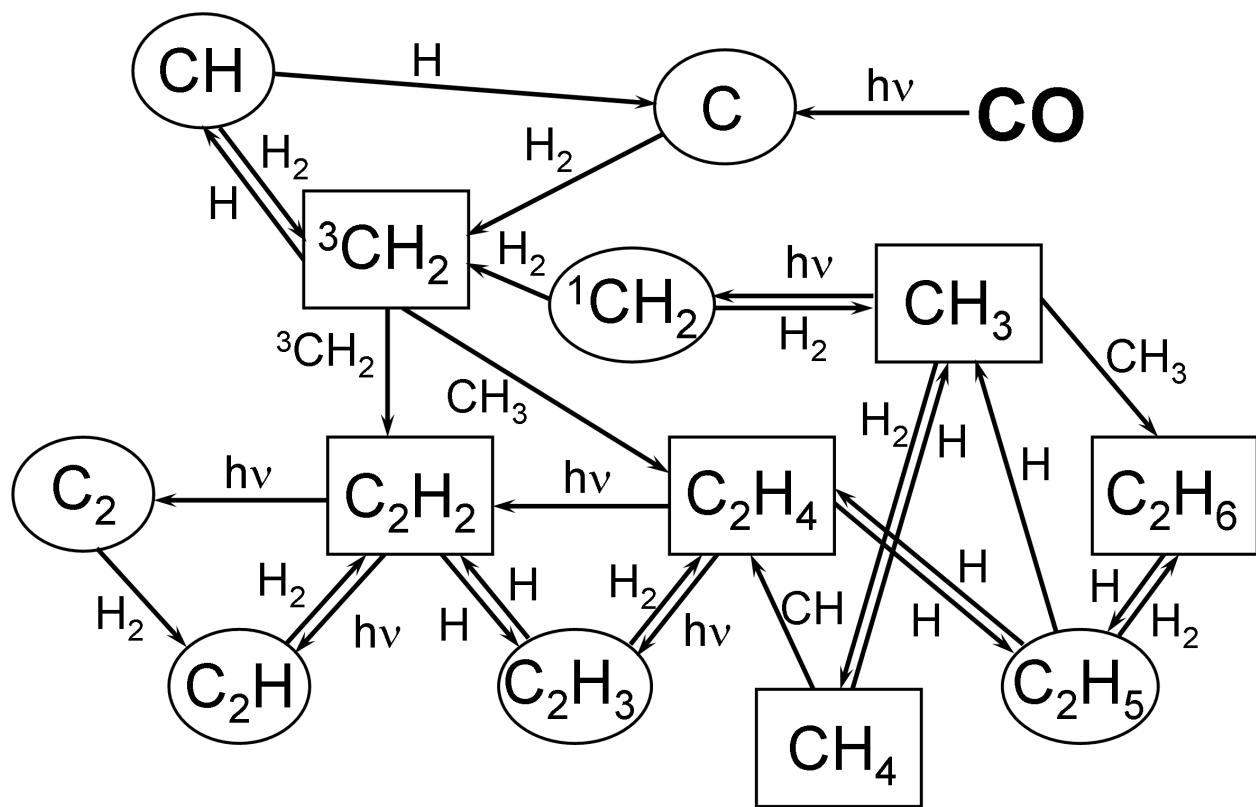


Fig. 2.— Major photochemical pathways for forming C and C<sub>2</sub> species.

Table 2. Mixing Ratios of CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub> for Models A-E at 0.1 mbar. Jupiter's Results at 2  $\mu$ bar are Included for Comparison.

Model <sup>a</sup>	CH <sub>4</sub>	C <sub>2</sub> H <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	Total <sup>b</sup>
Jupiter	$1 \times 10^{-3}$	$1 \times 10^{-5}$	$3 \times 10^{-8}$	$2 \times 10^{-5}$	1
A 1	$3 \times 10^{-6}$	$8 \times 10^{-7}$	$3 \times 10^{-8}$	$2 \times 10^{-11}$	$7 \times 10^{-4}$
<sup>d</sup> A 1	$2 \times 10^{-6}$	$6 \times 10^{-7}$	$3 \times 10^{-8}$	$1 \times 10^{-11}$	$7 \times 10^{-4}$
<sup>e</sup> A 1	$4 \times 10^{-6}$	$9 \times 10^{-7}$	$4 \times 10^{-8}$	$2 \times 10^{-11}$	$1 \times 10^{-3}$
<sup>f</sup> A 1	$5 \times 10^{-7}$	$1 \times 10^{-7}$	$4 \times 10^{-9}$	$1 \times 10^{-12}$	$1 \times 10^{-4}$
B 1	$9 \times 10^{-6}$	$2 \times 10^{-6}$	$1 \times 10^{-7}$	$6 \times 10^{-11}$	$2 \times 10^{-3}$
C 1	$5 \times 10^{-7}$	$1 \times 10^{-7}$	$4 \times 10^{-9}$	$1 \times 10^{-12}$	$7 \times 10^{-5}$
D 1	$3 \times 10^{-5}$	$5 \times 10^{-6}$	$5 \times 10^{-7}$	$3 \times 10^{-10}$	$7 \times 10^{-3}$
E 1	$3 \times 10^{-4}$	$2 \times 10^{-5}$	$6 \times 10^{-6}$	$4 \times 10^{-8}$	0.4
E 2	$2 \times 10^{-4}$	$9 \times 10^{-6}$	$1 \times 10^{-5}$	$1 \times 10^{-9}$	0.3
E 3	$4 \times 10^{-4}$	$2 \times 10^{-5}$	$1 \times 10^{-5}$	$9 \times 10^{-9}$	0.6

Note. — The hydrocarbons have maximum mixing ratios at about 0.1 mbar in the atmosphere of HD 209458b, while on Jupiter the maxima are at about 2  $\mu$ bar (see Figure 3).

<sup>a</sup>1: reference temperature profile (Seager & Sasselov 2000). 2: Barman et al. (2002) temperature profile. 3: Fortney et al. (2003) temperature profile.

<sup>b</sup>Total: column integrated abundances of hydrocarbons (C<sub>2</sub>H<sub>2</sub> + C<sub>2</sub>H<sub>4</sub> + C<sub>2</sub>H<sub>6</sub>) at < 2 bar. The abundance is normalized to  $2 \times 10^{-7}$  which is the value calculated in the atmosphere of Jupiter (e.g., Gladstone et al. 1996).

<sup>d</sup>Exponent of eddy-diffusion is taken to be 0.65.

<sup>e</sup>Eddy-diffusion is a factor of two smaller than the reference eddy-diffusion.

<sup>f</sup>Eddy-diffusion is a factor of ten greater than the reference eddy-diffusion.

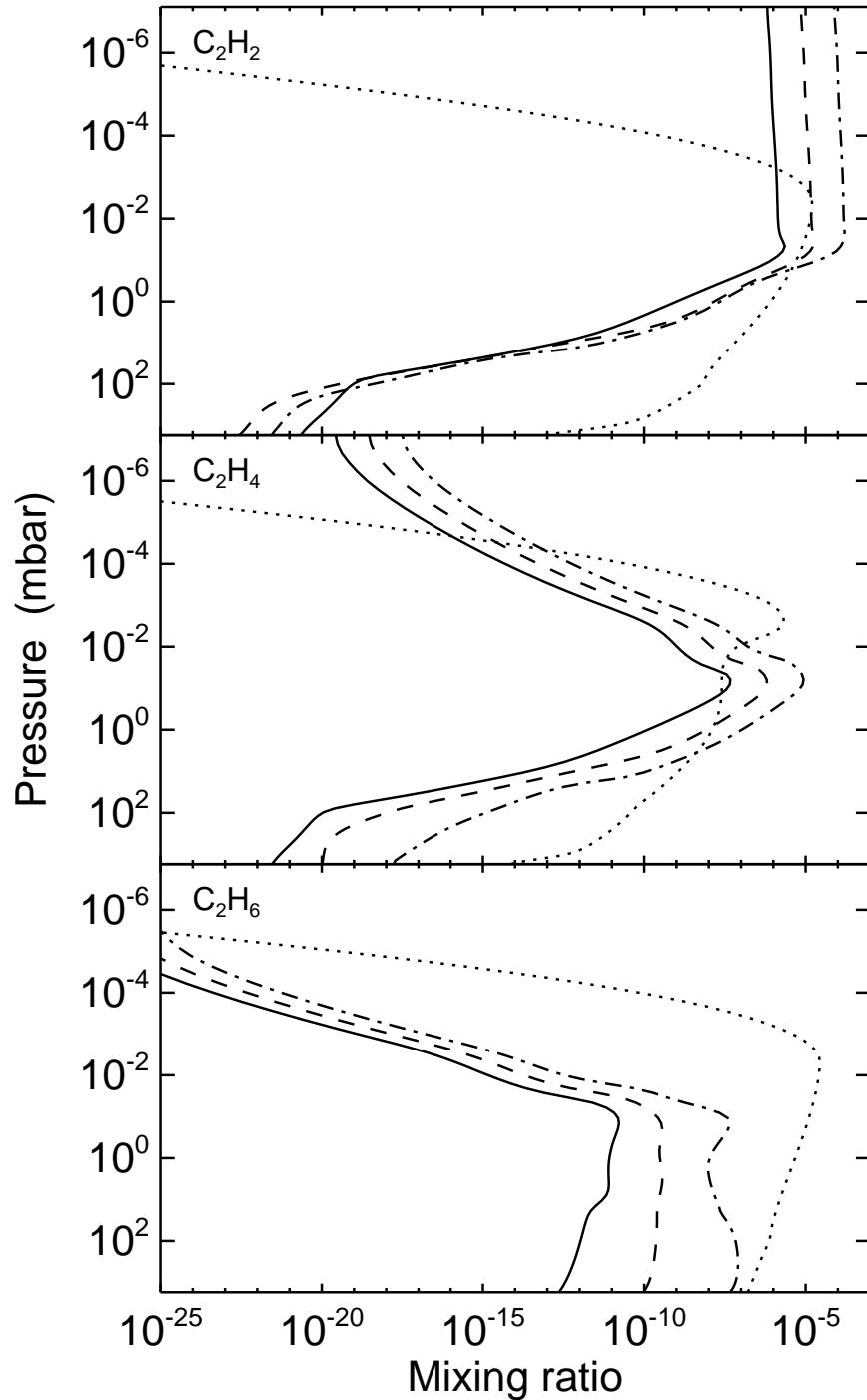


Fig. 3.— Comparison of volume mixing ratios of C<sub>2</sub>H<sub>2</sub> (upper panel), C<sub>2</sub>H<sub>4</sub> (middle panel), and C<sub>2</sub>H<sub>6</sub> (lower panel) for Models A, D, E, and Jupiter (solid, dashed, dash-dotted, and dotted lines, respectively). The high C<sub>2</sub>H<sub>2</sub> mixing ratio at the top of the atmosphere is due to the high photolysis rate of CO.

#### 4. Discussion

Using a simplified version of the Caltech/JPL KINETICS model, we have shown that the concentrations of the  $C_2H_{2n}$  species (see Table 2) are insignificant in the atmospheres of CEGPs. These  $C_2H_{2n}$  compounds are important sources for forming more complex  $C_xH_y$  species, such as benzene and PAHs, which will lead to the formation of hydrocarbon aerosols (e.g., Richter & Howard 2000, 2002). Although we have used a simplified photochemical model that captures the main reactions, we have tested Models A-E using the reference temperature profile (solid-line in Figure 1) incorporating the full version of hydrocarbon model by Gladstone et al. (1996). Even for this case, we find that the  $C_6H_6$  abundance for Model A is seven orders of magnitudes less than that of Jupiter and is two orders of magnitudes less for Model E. Sulfur and nitrogen containing compounds are other potential sources for aerosols and we plan to explore their photochemistry in a later paper.

The CEGPs are extremely close to the parent star; in such an extreme environment, the  $C_xH_y$  compounds will be lost either primarily by reactions with atomic hydrogen or also by photolysis. The production of atomic hydrogen is a consequence both of the high temperatures that allow the presence of  $H_2O$  vapor and of the high UV flux that causes photolysis of  $H_2O$ . Therefore, the lifetime of the  $C_xH_y$  compounds in the atmospheres of CEGPs is predicted to be much shorter than that on Jupiter. The lifetimes of the hydrocarbons are  $\lesssim 10^3$  s, which are significantly shorter than the simulated circulation timescale of  $\sim$ day (Showman & Guillot 2002; Cho et al. 2003). Hence the abundances of the hydrocarbons will be affected by a factor of ‘a few’ through the relatively longer lifetime of the atomic hydrogen ( $\sim$ 1 day, Liang et al. 2003).

The condensation temperatures for hydrocarbons (e.g.,  $C_4H_2$  and  $C_4H_{10}$ ) are below 200 K at  $\sim$ 1 mbar (Moses et al. 2000). These temperatures are far colder than expected in the atmospheres of CEGPs (Seager & Sasselov 2000; Barman et al. 2002; Fortney et al. 2003). Nevertheless, we verified this by considering the saturation profiles together with the temperature profiles and found that the required saturation pressure for CEGPs is far more than that present in the atmospheres.

Using the measured Rayleigh scattering cross sections of He and  $H_2$  (Chan & Dalgarno 1965; Ford & Browne 1973), the pressure level with optical depth unity is  $\sim$ 1 bar at 300 nm and increases rapidly at longer wavelengths (Rayleigh scattering cross section  $\propto \lambda^{-4}$ ). Without the shielding from the atmospheric aerosols and in the absence of high-temperature condensate clouds, we may be able to observe the atmospheric composition at short wavelengths up to the Rayleigh scattering limit.

In this letter, we have emphasized photolytically driven processes involving neutral

species. We have not considered the possibility of ion-neutral chemistry, such as that found in the polar region of Jupiter (Wong et al. 2003). This may be important in the atmospheres of CEGPs if the planet possesses a magnetic field. If the hydrocarbon aerosols can be formed in the polar region, then global circulation will redistribute them to lower latitudes. Stellar wind may be another source of energetic charged particles that could result in the formation of aerosols. Another subject not addressed in this work is the formation of aerosols by heterogeneous nucleation in the presence of pre-existing solid dust grains. In this case, the formation of aerosols would be sensitive to the amount of dust particles in the atmosphere.

Additionally, we find that the mixing ratios of C, O, S, and  $C_2H_2$  (other than H) are high at the top of the atmosphere, implying that these particles can readily escape. The recent detection of C and O in the extended upper atmosphere of HD 209458b by Vidal-Madjar et al. (2004) supports this assertion and we comment that hydrodynamically escaping atmospheric species will yield new information on the evolution of CEGPs.

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